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The acylated cellobiose materials of the present invention may be used as a sole or primary structurants or may be used as minor or supplementary structurant in conjunction with one or more of the classes of structurants that are mentioned hereinafter. By way of example, the invention structurants can be used together with an acylated cellobiose described in PCT/GB 00/01228, in which the anomeric acyl group is the same as at least some of the other acyl groups, ie  $R = R'$ , such as cellobiose octanonanoate, especially, cellobiose octadecanoate.

It is especially desirable to employ acylated cellobiose materials identified herein (CHMEs) in which all the R substituents are identical and are n-nonyl or particularly n-octyl and at least 75% of substituents at the anomeric carbon are  $R'$  (ie at least 75 molar% acylation at the anomeric position) and = cyclohexyl, phenyl, naphthyl or methyl and particularly cyclohexyl. Such especially desirable CHMEs preferably are at least 80 molar% in the  $\beta$  anomeric form.

#### Material Preparation

One convenient and general method for making the acylated cellobiose compounds of the present invention comprises the step of transesterifying a corresponding acylated cellobiose in which the acyl substituents -COR and -COR' are identical. Such a process in practice can be two step, the first step of which comprises preparing an octaesterified cellobiose, for example by a process as described hereinbelow. The

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second step of such a process comprises reacting the octaester with an acylating agent containing a -COR' residue, capable of displacing the residue -COR, if needed in the presence of a strong acylating catalyst. The resultant product often comprises a proportion of residual R-CO- residues at the anomeric carbon atom.

A related method comprises acylating the corresponding partially acylated cellobiose with an acylating agent containing a -COR' residue, where needed in the presence of an acylating catalyst, the anomeric carbon being partly or preferably wholly or substantially wholly substituted by an hydroxyl group. Such a substrate can be obtained, for example, by deacylating wholly or partly a cellobiose octester. Consequently, the invention mixed ester cellobiose compounds can be made in a three step process comprising the steps of first making an octaester in which the acyl substituent -COR' at the anomeric carbon is the same as at the other cellobiose carbons, R-CO-, secondly removing the anomeric acyl substituent, and then re-acylating at the anomeric position with a different acyl substituent.

In one way of carrying out the first step, be it for either the two or three step processes indicated above, cellobiose (commonly D-(+)-cellobiose) is reacted with a molar excess of an acylating agent, often a substantial excess, such as an acid chloride,  $\text{RCOCl}$ , carboxylic acid  $\text{RCO}_2\text{H}$  or acid anhydride  $(\text{RCO})_2\text{O}$  and, where necessary, an acylation catalyst. The R groups are as hereinbefore described. For

- example, when using an acid as acylating agent, the catalyst can desirably be derivable from an acid having a low  $pK_a$  such as an anhydride  $(R''CO)_2O$ , often in a significant molar excess. The  $R''$  group is desirably a polychlorinated or preferably polyfluorinated alkyl, such as trifluoromethyl.
- 5 The acylating agent, eg carboxylic acid, is preferably employed at a mole ratio to the cellobiose in the range of at least 50:1 and especially from 60:1 to 100:1. The catalyst is preferably employed with the acid at a mole
- 10 ratio to the cellobiose of at least 20:1 and particularly from 22:1 to 50:1. The acylation is desirably conducted at an elevated temperature such as above  $70^\circ C$  and especially approximately  $100^\circ C$  for a period of at least 2 hours and especially from 3 to 10 hours. The resultant product is
- 15 substantially or completely acylated, that is to say that at least 90% of the acylatable hydroxyl groups on the cellobiose have been acylated and often at least 95% acylated.
- 20 In a variant of the first step, the cellobiose (commonly D-(+)-cellobiose) is reacted with a molar excess of an acylating agent, often a significant excess, such as an acid chloride,  $RCOCl$ , in solution in a volatile chlorohydrocarbon such as chloroform, the presence of an excess of a strong
- 25 base catalyst, such as pyridine, and most preferably in a dry, inert atmosphere. Preferably, the acylating agent is employed in a mole ratio to the cellobiose in the range of from 12:1 to 24:1, from 1.5 to 3 times a stoichiometric amount for octa-acylation. The base catalyst is commonly
- 30 employed in a mole ratio to the cellobiose of from 6:1 to